

Studies of the defect structure from the calculations of optical and electron paramagnetic resonance spectra for Ni^{2+} centre in $\alpha\text{-LiIO}_3$ crystal

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Abstract. By calculating the optical spectrum band positions and EPR parameters (g factors, g_{\parallel} , g_{\perp} and zero-field splitting D) by diagonalizing the complete energy matrix of $3d^8$ ions in trigonal symmetry, the defect structure of Ni^{2+} centre in $\alpha\text{-LiIO}_3$ crystal is studied. It is found that to reach the good fits of optical and EPR data between calculation and experiment, the Ni^{2+} ion should shift by $\Delta z \approx 0.298 \text{ \AA}$ along C_3 -axis and the O^{2-} ions between the Ni^{2+} ion and Li^+ vacancy (V_{Li}) should be displaced away from the V_{Li} by $\Delta x \approx 0.097 \text{ \AA}$ because of the electrostatic interaction. The results are discussed.

Keywords. Optical spectra; electron paramagnetic resonance; defect structure; Ni^{2+} ; $\alpha\text{-LiIO}_3$.

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1. Introduction

$\alpha\text{-LiIO}_3$ crystal is used in electronic and electro-optical devices because of its non-linear, optical, photoelastic and electro-optical properties [1–5]. Since transition metal ($3d^n$) impurities can strongly influence the optical properties and photorefractive effects of the crystal, the studies of defect structure of these $3d^n$ impurity centres in $\alpha\text{-LiIO}_3$ have attracted considerable interest [6–11]. The EPR spectra (characterized by EPR or spin-Hamiltonian parameters) and also the optical spectra of a $3d^n$ impurity in crystals are sensitive to its immediate environment. It is

natural to study the defect structure of a $3d^n$ impurity in crystals by calculating its EPR parameters and the optical spectrum band positions. There are two theoretical methods which can be used to calculate EPR parameters and also optical spectrum band positions of $3d^n$ ions in crystals: one is the complete diagonalization (of energy matrix) method (CDM) and the other is the perturbation theory method (PTM) [12,13]. Since CDM can consider the contributions to EPR parameters from all the $3d^n$ excited states within the crystal-field framework, it can provide more accurate calculated results of EPR parameters (and also optical spectrum) than PTM in some cases (e.g., the perturbation formulas are of low order). In this paper, we calculate the EPR parameters (g factors g_{\parallel} , g_{\perp} and zero-field splitting D) and also the optical spectrum band positions for Ni^{2+} ion in $\alpha\text{-LiIO}_3$ by using CDM. From the calculation, the defect structure of Ni^{2+} impurity centre in $\alpha\text{-LiIO}_3$ is estimated. The results are discussed.

2. Calculation

Ni^{2+} ion in $\alpha\text{-LiIO}_3$ crystal substitutes for Li^+ ion and is at a trigonal site [14,15]. The excess charge is compensated by a vacancy (V_{Li}) of the nearest Li^+ ion on the C_3 -axis above or below the Ni^{2+} ion. In $\alpha\text{-LiIO}_3$ crystal, the Li^+ ion is arranged eccentrically in octahedral LiO_6 cluster, i.e., Li^+ ion is displaced by about 0.02 Å along C_3 -axis from a plane half-way between those formed by the O^{2-} ion [16]. So the V_{Li} above and below the impurity ion can form two non-equivalent impurity centres A and B. This point was found for similar divalent $3d^n$ ions Mn^{2+} and Co^{2+} in $\alpha\text{-LiIO}_3$ crystals [6,7]. For Ni^{2+} in $\alpha\text{-LiIO}_3$ crystal, however, only one Ni^{2+} centre has been found [14,15]. Considering that in the EPR spectra, the intensity ratios of centre B to centre A are about 4 and 20 for Mn^{2+} [6] and Co^{2+} [7] in $\alpha\text{-LiIO}_3$, respectively, we can assume reasonably that Ni^{2+} ion in $\alpha\text{-LiIO}_3$ is at site B (i.e., V_{Li} is below the Ni^{2+} ion). The effective charge of V_{Li} is negative, and the Ni^{2+} ion and the O^{2-} ions in the vicinity of V_{Li} should be displaced by Δz and Δx , respectively (see figure 1), owing to the electrostatic interactions between these ions and V_{Li} . The defect structure of Ni^{2+} impurity centre in $\alpha\text{-LiIO}_3$ can be characterized by the displacements Δz and Δx . These displacements can be estimated by calculating the EPR and also optical spectral data from CDM.

For $3d^8$ (Ni^{2+}) ions in trigonal symmetry, the Hamiltonian can be expressed as

$$H = H_f(B, C) + H_{\text{SO}}(\zeta) + H_{\text{CF}}(Dq, D\sigma, D\tau), \quad (1)$$

where the three terms are the free-ion term (including the Racah parameters B and C), spin-orbit interaction term (related to the spin-orbit coupling parameter ζ) and the crystal-field interaction term (characterized by the crystal-field parameters Dq , $D\sigma$, $D\tau$). In terms of the strong field basis functions [17], the 45×45 complete energy matrix for $3d^8$ (or $3d^2$) ions in trigonal symmetry is established [13,18]. Diagonalizing the energy matrix, the energy levels (and hence the optical spectrum band positions) and the wave functions $|(t_{2g}^6 e_g^2)^3 A_{2g}, M_s\rangle$ of ground state can be acquired. By the aid of the equivalence between spin-Hamiltonian parameters and the Zeeman terms, we have

Ni^{2+} centre in α - $LiIO_3$ crystal

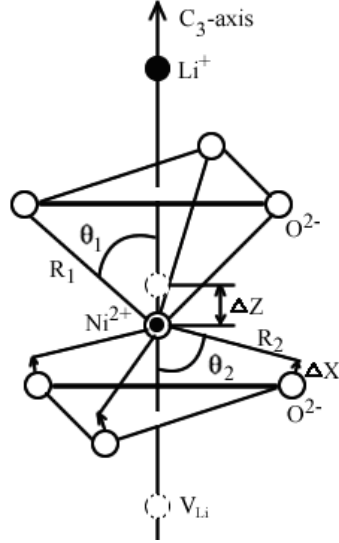


Figure 1. Defect structure of Ni^{2+} centre in α - $LiIO_3 : Ni^{2+}$ crystal.

$$\begin{aligned}
 g_{\parallel} &= \langle (t_{2g}^6 e_g^2)^3 A_{2g}, 1, e_2 | kL_z + 2.0023S_z | (t_{2g}^6 e_g^2)^3 A_{2g}, 1, e_2 \rangle', \\
 g_{\perp} &= \sqrt{2} \langle (t_{2g}^6 e_g^2)^3 A_{2g}, 1, e_2 | kL_x + g_e S_x | (t_{2g}^6 e_g^2)^3 A_{2g}, 0, e_2 \rangle', \\
 D &= E(|(t_{2g}^6 e_g^2)^3 A_{2g}, \pm 1, e_2 \rangle') - E(|(t_{2g}^6 e_g^2)^3 A_{2g}, 0, e_2 \rangle'), \quad (2)
 \end{aligned}$$

in which L_j ($j = x, y, z$) and S_j are the operators of orbit and spin angular momentums, respectively. $E(|(t_{2g}^6 e_g^2)^3 A_{2g}, M_s \rangle')$ are the energy levels concerning the corresponding states.

Because of the covalence reduction effect for $3d^n$ clusters in crystals, the Racah parameters B , C and spin-orbit coupling parameter ζ should be smaller than the corresponding parameters B_0 , C_0 and ζ_0 in free state [17,19,20]. A covalence reduction factor $N (< 1)$ is introduced to represent the effect. Thus, we have [20–22]

$$B \approx N^4 B_0, \quad C \approx N^4 C_0, \quad \zeta \approx N^2 \zeta_0, \quad k \approx N^2. \quad (3)$$

For free Ni^{2+} ion, we have [18]

$$B_0 \approx 1084 \text{ cm}^{-1}, \quad C_0 \approx 4831 \text{ cm}^{-1}, \quad \zeta_0 \approx 649 \text{ cm}^{-1}. \quad (4)$$

The crystal-field parameters can be calculated from the superposition model [23]. From the model, we obtain

$$\begin{aligned}
 Dq &= \frac{-3}{\sqrt{2}} \bar{A}_4(R_0) \sum_{i=1}^2 \left(\frac{R_0}{R_i} \right)^{t_4} \sin^3 \theta_i \cos \theta_i, \\
 D\sigma &= \frac{3}{7} \bar{A}_2(R_0) \sum_{i=1}^2 \left(\frac{R_0}{R_i} \right)^{t_2} (3 \cos^2 \theta_i - 1),
 \end{aligned}$$

$$D\tau = \frac{1}{7}\bar{A}_4(R_0) \sum_{i=1}^2 \left(\frac{R_0}{R_i}\right)^{t_4} \times (35 \cos^4 \theta_i - 30 \cos^2 \theta_i + 7\sqrt{2} \sin^3 \theta_i \cos \theta_i), \quad (5)$$

where the power-law exponents are $t_2 \approx 3$ and $t_4 \approx 5$ [21–23]. $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters with the reference distance R_0 [$\approx \bar{R} \approx \frac{1}{2}(R_1 + R_2)$]. $\bar{A}_2(R_0) \approx (8-12)\bar{A}_4(R_0)$ is obtained for $3d^n$ ions in many crystals [22,24–26] and we take $\bar{A}_2(R_0) \approx 9\bar{A}_4(R_0)$ here. R_i ($i = 1$ and 2) are the impurity–ligand distances and θ_i are the angles between R_i and C_3 -axis (see figure 1). They can be calculated from the corresponding structure data R_i^0 and θ_i^0 in the host α -LiIO₃ crystal and the displacements Δz and Δx . From the crystallographic data [16], we have $R_1^0 \approx 2.11$ Å, $R_2^0 \approx 2.13$ Å, $\theta_1^0 \approx 52.9^\circ$ and $\theta_2^0 \approx 52.05^\circ$. The unknown parameters N , $\bar{A}_4(R_0)$, Δz and Δx are the adjustable parameters. They are obtained by fitting the calculated optical spectrum band positions and EPR parameters. Diagonalizing the above matrix, we find that to reach the good fits between calculation and experiment,

$$N \approx 0.958, \quad \bar{A}_4(R_0) \approx 550 \text{ cm}^{-1}, \quad \Delta z \approx 0.298 \text{ Å}, \quad \Delta x \approx 0.097 \text{ Å}. \quad (6)$$

The comparisons of the calculated optical band positions and EPR parameters with the observed values are shown in tables 1 and 2.

Table 1. The energy levels (and hence the optical absorption band positions) of Ni²⁺ ions in α -LiIO₃ crystal.

		V _{cub}			Expt. [27]		V _{tri}			Expt. [27]	
		Spinors	Calc.				Spinors	Calc.			
$t_{2g}^6 e_g^2$	${}^3A_{2g}$	3E_g	E_g	-3.2102^a	-3.21^a	$t_{2g}^5 e_g^3$	${}^1T_{2g}$	${}^1A_{1g}$	A_{1g}	21536	
		${}^3A_{2g}$	A_{1g}	0	0			1E_g	E_g	21835	
$t_{2g}^5 e_g^3$	${}^3T_{2g}$	3E_g	E_g	7437		$t_{2g}^4 e_g^4$	${}^3T_{1g}$	3E_g	E_g	23441	
		${}^3A_{1g}$	A_{2g}	7519				${}^3A_{2g}$	A_{1g}	23694	
		3E_g	E_g	7646	7600			${}^1A_{1g}$	A_{1g}	23726	
		3E_g	E_g	7964				${}^3T_{1g}$	E_g	24366	
		${}^3A_{1g}$	A_{2g}	8027				3E_g	E_g	24469	
$t_{2g}^5 e_g^3$	${}^3T_{1g}$	${}^3A_{1g}$	A_{2g}	8131				${}^3A_{2g}$	A_{1g}	24574	
		${}^3A_{2g}$	A_{1g}	12208				${}^3A_{2g}$	A_{1g}	24700	
		${}^3A_{2g}$	A_{1g}	12588	12480	$t_{2g}^5 e_g^3$	${}^1T_{1g}$	${}^1A_{1g}$	A_{1g}	26818	
		3E_g	E_g	12717				1E_g	E_g	27103	
		3E_g	E_g	13194		$t_{2g}^4 e_g^4$	1E_g	1E_g	E_g	32358	
		3E_g	E_g	13472		$t_{2g}^4 e_g^4$	${}^1T_{2g}$	1E_g	E_g	33026	
$t_{2g}^6 e_g^2$	1E_g	${}^3A_{2g}$	A_{1g}	13628	13800			${}^1A_{1g}$	A_{1g}	33339	
		1E_g	E_g	15304		$t_{2g}^4 e_g^4$	${}^1A_{1g}$	${}^1A_{1g}$	A_{1g}	59675	

^aObtained from EPR spectra [15].

Table 2. The EPR parameters of Ni²⁺ ions in α -LiIO₃ crystal.

	D (cm ⁻¹)	g_{\parallel}	g_{\perp}
Calc.	-3.2102	2.2802	2.2561
Expt. [15]	-3.21	2.280	2.257

3. Discussion

From tables 1 and 2, it can be seen that the calculated optical spectrum band positions and EPR parameters are in good agreement with the experimental values, suggesting that these spectral data can be explained rationally by CDM.

The calculated displacements Δz of Ni²⁺ ion and Δx of O²⁻ ions between Ni²⁺ and V_{Li} in direction are consistent with the expectation based on the electrostatic interactions. In addition, similar displacements were found from the radio-frequency discrete saturation (RFDS), ENDOR and EPR studies [6,7,10,11] for the other divalent 3dⁿ ions Mn²⁺ (where $\Delta z \approx 0.31 \text{ \AA}$, $\Delta x \approx 0.28 \text{ \AA}$ [6,10]) and Co²⁺ (where $\Delta z \approx 0.19 \text{ \AA}$, $\Delta x \approx 0.49 \text{ \AA}$ [7,11]) in α -LiIO₃ crystals. So, the above displacements Δz and Δx and hence the defect structure of Ni²⁺ impurity centre in α -LiIO₃ crystals can be regarded as reasonable. It appears that information on the defect structure of a 3dⁿ impurity in crystals can be obtained by calculating its optical and EPR spectrum parameters.

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